A Computer Aided System for Correlation

and Prediction of Phase Equilibrium Data

T. L. Nielsen & R. Gani*

CAPEC, Department of Chemical Engineering, Technical University of Denmark,

DK-2800 Lyngby, Denmark, *E-mail: rag@kt.dtu.dk

Abstract

Modelling, simulation and design of chemical processes need accurate and reliable estimation of the properties of the mixtures present in the process. In these situations the property models are in a "service" role where they supply the needed properties only when requested. Due to the solution procedures employed in simulation and design, the property models are required to have well-behaved and continuous derivatives for these problems to convergence. Furthermore, in process optimisation the second and third order derivatives of the property models must exist for solution approaches based on mathematical programming. This paper describes the development of a computer aided system for the systematic derivation of appropriate property models to be used in the service role for a specific problem. As a first step, a library of well-known property models has been developed and a feature for parameter estimation has been added so that for any selected model, the necessary model parameters can be estimated, fine-

tuned and/or converted from one model to another model. Also, the property derivatives are validated and verified for thermodynamic and mathematical consistency.

Introduction

Modelling has become a routine activity at almost all levels of chemical engineering, from process synthesis and design, through process operation and control, to planning and analysis. At all these levels, different types of mathematical models are needed and solved. Even though modelling plays a very important role, development of computer aided techniques that can aid in the systematic derivation of the appropriate mathematical model is relatively new.

In problems related to process simulation and design, property models are used to calculate pure component and mixture properties. One of the most commonly used mixture properties are those related to the prediction of the phase behaviour. Gani and O'Connell [1] have pointed out that for the same process, property models of different formulation, complexity and accuracy may be used to solve different process problems. They show that property models play three roles in chemical process and product design. The first role is the service role, where the models provide property values only when requested. The second role is the service/advise role, where in addition to the service role, property models play an advise role by providing explicit or implicit target values for those properties that can be manipulated to match some design objectives. Finally, there is the service/advise/solve role, where properties can suggest alternative and better strategies for solving process problems.

This paper highlights the "service" role of the property models through a computer aided system for correlation and prediction of phase equilibrium related mixture properties.

The Service Role of Property Models

Property models play a service role in the solution of most simulation problems. For instance, in the simulation of a distillation column the system conditions (temperature, pressure and composition of liquid and vapour phase) are parsed to selected property models that respond by supplying numerical values of the equilibrium constants and enthalpies that are needed to solve the mass- and energy balances. Property models are "asked" to supply property values numerous times during the iteration to the solution and since property model regularly are mathematical complex they can be the main contribution to the computational time. Furthermore, property models are often the cause of non-linear process models and therefore causing difficulties in achieving convergence [1]. In fact, if the first order derivatives of the property models are not continuous the simulation will not convergence. Consequently, in process design and simulation property models are required to have continuous first order derivatives. Even though, in general, most property models satisfy this there are models or values of the model parameters that can cause discontinuity.

A very simple example is the well-known van Laar activity coefficient model [2] that for certain values of the model parameters will have discontinuities.

$$\frac{G^E}{R \cdot T} = \frac{x_1 \cdot x_2 \cdot A}{x_1 \cdot \left(\dfrac{A}{B}\right) + x_2} \tag{1}$$

The two parameters, A and B, in the van Laar model must satisfy the constraint A∗B>0 for the activity coefficients and the derivatives to be continuous in the entire composition range. An example where this constraint is not satisfied is the parameters reported by Gmehling for the water-aniline mixture [3].

Normally in simulation and design problems one or more of the state variables (e.g. temperature and/or vapour composition) are unknown and an iterative procedure generates temporary values for these variables. Thus, property models must be continuous and well behaved at conditions that are not "real" to achieve convergence [1]. Examples of property models that can cause discontinuities in "unreal" conditions are equation of states (EOS). For instance, if non-condensable compounds are present in the mixture the EOS may fail to give the required liquid root during the iterative solution of a flash calculation.

In process optimisation property models are required to have not only continuous and well-behaved first order derivatives but also continuous second and even third order derivatives. This is illustrated in the following example.

Consider the flash drum in Figure 1, where a feed stream is split in a vapour and liquid stream by the heat addition, Q, to the drum. The flash drum is capable of operating in a range of temperatures and pressures, however the fraction of the feed that leaves the flash drum as vapour, β, must be kept constant. Figure 2 shows the minimisation problem, where in the possible temperature and pressure range the heat addition will be minimised subject to the constraints (*i*) to (*vi*). The first constraint (*i*) is specifying the constraint on β, (*ii*) and (*iii*) are specifying the temperature and pressure range, (*iv*) is the mass balances, (*v*) the equilibrium constraints and (*vi*) the energy balance.
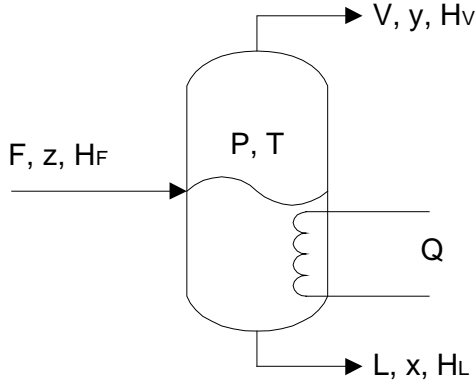
$$\min_{P,T} Q$$

$$\text{s.t.} \quad \beta = \text{constant value} \qquad (i)$$
$$T \in \left[T_{lower}, T_{upper} \right] \qquad (ii)$$
$$P \in \left[P_{lower}, P_{upper} \right] \qquad (iii)$$
$$F \cdot z_i = V \cdot y_i + L \cdot x_i \; ; i = 1, NC \quad (iv)$$
$$y_i = K_i(P, T, x, y) \cdot x_i \; ; i = 1, NC \quad (v)$$
$$F \cdot H_F + Q = V \cdot H_v + L \cdot H_L \qquad (vi)$$

Figure 1: Flash drum.   **Figure 2:** Minimisation of heat addition.

To solve this optimisation problem the Lagrange function is defined as [4]:

$$L(X, \lambda, \mu) = Q(X) + \sum h_i(X) \cdot \lambda_i + \sum g_i(X) \cdot \mu_i \qquad (2)$$

where h_i are the equality constraints (*i*), (*iv*) to (*vi*) in the form $h_i = 0$, g_i are the inequality constraints (*ii*) and (*iii*) in the form $g_i \leq 0$, λ_i and μ_i are the lagrange multiplier for the equality and inequality constraints, respectively and $X = \{F, z_i, H_F, P, T, V, y_i, H_v, L, x_i, H_L\}$.

At the optimal condition the necessary eq. (3) and sufficient eq. (4) Kuhn-Tucker conditions must be satisfied.

$$\nabla L_X(X^*, \lambda^*, \mu^*) = \nabla Q(X^*) + \nabla h(X^*) \cdot \lambda^* + \nabla g(X^*) \cdot \mu^* = 0$$
$$\mu^T \cdot g(X^*) = 0, \quad \mu \geq 0 \qquad (3)$$
$$g(X^*) \leq 0, \quad h(X^*) = 0$$

$$\nabla_{XX}^2 L(X^*) = \text{positive definite Hessian} \qquad (4)$$

Continuous first and second order derivatives of the Lagrange function is required for the optimisation to reach a solution and hence requires continuous first and second order derivatives of the constraints (*i*) to (*vi*). Thus the property models that are used to calculate the equilibrium constants and the enthalpies must be twice differentiable. Since enthalpy is commonly calculated as the sum of the ideal gas enthalpy plus the

5

residual enthalpy and that residual enthalpy is the temperature derivative of the fugacity coefficient eq. (5), then the third order derivatives with respect to temperature must be continuous for the Hessian of the Lagrange function to be continuous.

$$H^R = -R \cdot T^2 \cdot \left(\frac{\partial \ln \varphi}{\partial T} \right)_{P,x} \tag{5}$$

The role of property models in the service role is therefore more comprehensive than "just" providing property values. For property models to be used in process simulation/design and optimisation the behaviour of the derivatives are of utmost importance in both "real" and "unreal" conditions.

Computer Aided System

A computer aided system for the systematically derivation of problem specific property models that satisfy the service role is under development. The necessary steps in the generation of problem specific models can be summarised as: selection or generation of property model, search and analysis of experimental data to obtain the model parameters and validation of the generated model.

Step 1: Selection of Property Model

Gani and O'Connell [5] have developed a knowledge-based system for the selection of appropriate property models. Given the compounds, the system conditions and the type of operation (flash, distillation etc.) a list of feasible property models is generated. To be able to accommodate these suggestions a library of the most common property models used for phase equilibrium calculations have been developed. The library includes both

equations of state and excess Gibbs energy models. Examples of excess Gibbs energy models included in the library are Wilson, NRTL, UNIQUAC and UNIFAC, but also electrolyte models such as Pitzer, Elec-NRTL and extended UNIQUAC have been included. Examples of equations of state are the classical van der Waals type equation of states (Redlich-Kwong, Soave- Redlich-Kwong, Peng-Robinson etc.) with classical mixing rules. Models using various combinations of EOS and excess Gibbs energy models to generate mixing rules such as Huron-Vidal, MHV2 and Wong-Sandler are also possible [6]. Analytical derivatives with respect to temperature, pressure and composition are provided for all the models.

The models in the library have been derived as objects or as a collection of objects and are therefore very flexible. Hence, in the case where none of the common property models are satisfactory it is possible to generate new models by combination of different objects to arrive at a model that is capable of describing the system. For example, consider the generalised cubic equation of state in Figure 3 that for certain values of δ_1 and δ_2 reduced to the known equation of states such as the Redlich-Kwong EOS for $\delta_1=1$ and $\delta_2=0$.

$$P = \frac{R \cdot T}{v - b} - \frac{a_c \cdot \alpha(T)}{(v + \delta_1 \cdot b) \cdot (v + \delta_2 \cdot b)}$$

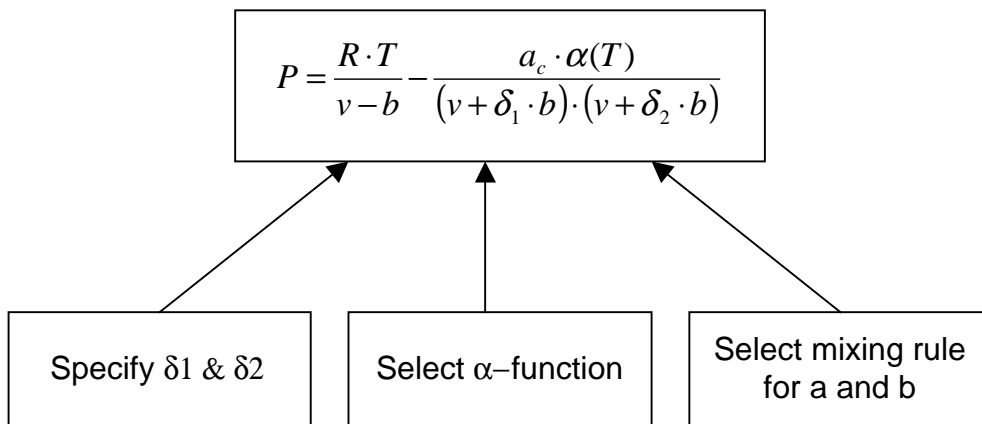Specify δ1 & δ2   Select α–function   Select mixing rule for a and b

Figure 3: Generation of problem specific equation of state.

A new equation of state can be constructed by specifying other values for δ_1 and δ_2 (for example to get a better representation of the liquid density [7]), select an expression for the α-function to match the vapour pressure of the pure components and to choose a mixing rule for the a- and b- parameter.

In addition to mixture property models correlations for pure component properties that are of importance for phase equilibrium calculations are included in the model library (such as saturated vapour pressure). Together with the mixture models they provide the complete description of the property behaviour.

Step 2: Parameter Estimation

When the appropriate property model has been selected the next step is to obtain the necessary model parameters for the model to mimic the behaviour of the system. Normally the parameters are regressed to experimental data such as vapour-liquid equilibrium data and excess/residual properties. An efficient algorithm for the identification of the adjustable model parameters and the regression of those to various types of experimental data has been developed to handle any property model in the library. The algorithm is connected to the CAPEC database that contains a large collection of binary and ternary equilibrium data [8] so that the necessary data can be made available for the optimisation algorithm. If experimental data are not available for a binary subset of the mixture an appropriate predictive model can be used to generate the missing data. Many features such as sensitivity analysis of the model parameters to determine the most sensitive parameters have been added to enhance the quality of the fit. Several techniques are used to validate the fit such as residual plots and the calculation of standard deviations.
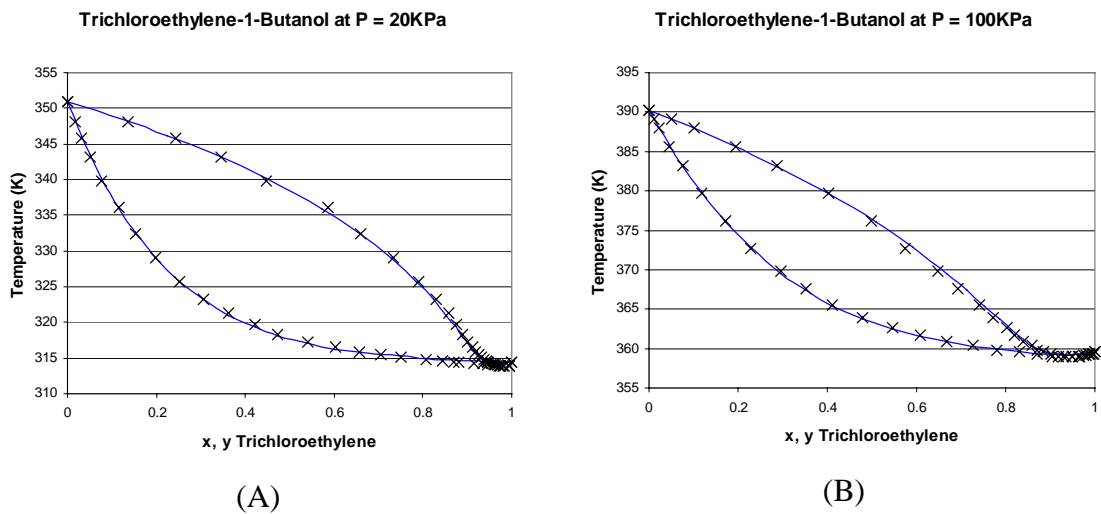
Figure 4: VLE for Trichloroethylene - 1-butanol mixture at 20 KPa and 100 KPa.

An example of the regression is shown for the trichloroethylene - 1-butanol system in Figure 4, where UNIQUAC parameters were regressed simultaneously to isobaric data at 20 KPa and 100 KPa (assuming ideal gas behaviour). As seen, the UNIQUAC model (the solid lines) describes the experimental data (the crosses) quite well. Prior to the regression of the UNIQUAC parameters the correlation for the saturated vapour pressure of trichloroethylene and 1-butanol was fine-tuned to match the experimental vapour pressures at 20 KPa and 100 KPa. To avoid possible errors in subsequent simulation and/or design problems the obtained UNIQUAC parameters should be used together with the fine-tuned saturated vapour correlation. When the computer aided system is used to derive a model for this system the problem is considered as a whole and the generated model is a combination of both pure component and mixture property models that are needed to describe the specified system. Thus, in this case the generated model is the UNIQUAC model with the fitted parameters plus ideal vapour phase plus the vapour pressure correlation with the fine-tuned parameters.

Step 3: Validation of Generated Model

Since the model library can be used to generate new mixing rules etc. it is necessary to check whether the generated model is mathematically and thermodynamically consistent. The derivatives are used to verify thermodynamic consistency for example by checking if the model satisfy the Gibbs-Duhem equation [2] and other tests as suggested by Mollerup and Michelsen [10] and Michelsen and Kistenmacher [11]. Also, a method to verify that the property model is satisfying the "service" role requirements is under development.

Conclusion

The requirements of property models in the service role have been identified and it has been shown that derivatives of property models play an important role in process simulation, design and optimisation. A computer aided system for the systematic derivation of property models is an useful tool for chemical engineers for setting up more accurate and thermodynamically consistent property models. The emphasis so far has been in the development of a flexible and object oriented property model library with most of the well-known mixture property models and the development of an efficient parameter estimation algorithm. The graphical interface of the tool makes it very easy to visualise the important problem solution steps as well as to use the tool for efficient solution of problems.

The next steps in the development of the computer aided system are the more systematic and more detailed validation of the generated models and to further expand the tool to be able to handle electrolyte systems.

Finally, the framework for the developed computer program package also serves as an excellent education tool.

List of Symbols

A, B   van Laar model parameters.

a_c Critical attraction parameter in equation of state.

b   Co-volume in equation of state.

F   Flowrate offeed stream.

G^E Excess Gibbs energy.

L   Flowrate of liquid stream.

H   Enthalpy.

K_i Equilibrium constant for compound i.

NC   Number of compounds in mixture.

P   Pressure.

Q   Heat addition in flash drum.

R   The gas constant.

T   Temperature.

V   Flowrate of vapour stream.

v   Molar volume.

x_i Composition of compound i in liquid phase.

y_i Composition of compound i in vapour phase.

z_i Composition of compound i in feed stream.

Greek letters

α   Temperature dependence of the attraction parameter.

β   Vapour flowrate divided with feed flowrate.

δ_1, δ_2 Parameter in Figure 3.

φ Fugacity coefficient of mixture.

λ_i Lagrange multiplier for equality constrain i.

μ_i Lagrange multiplier for inequality constrain i.

subscripts

F   Feed stream.

L   Liquid phase.

V   Vapour phase.

References

[1]   R. Gani and J. P. O'Connell, Properties and CAPE: From present uses to future challenges, ESCAPE-9 meeting, Budapest, May, 1999.

[2]   J. M. Prausnitz, R. N. Lichtenthaler, E. Gomez de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 2. ed., Prentice-Hall, 1986.

[3]   J. Gmehling & U. Onken, Vapor-Liquid Equilibrium Data Collection, Chemistry Data Series, vol. I, part 1, p. 502, DECHEMA, 1977.

[4]   L. T. Biegler, I. E. Grossman, A. W. Westerberg, Systematic Methods of Chemical Process Design, Prentice Hall PTR, 1997.

[5]   R. Gani, J. P. O'Connell, Comput. Chem. Eng., 13, 397-404, 1989.

[6]   H. Orbey and S. I. Sandler, Modeling Vapor-Liquid Equilibria. Cubic Equations of State and Their Mixing Rules, Cambridge University Press, 1998.

[7]   G. Schmidt and H. Wenzel, A Modified van der Waals Type Equation of State, Chemical Engineering Science, vol 35, 1503-1512, 1980.

[8]   T. L. Nielsen, J. Abildskov, P. M. Harper, I. Papaeconomou & R. Gani, The CAPEC Database, presented at the 14th Symposium on Thermophysical Properties, Boulder, Colorado, June 25-30, 2000.

[9]   A. Dejoz, V. González-Alfaro, P. J. Miguel and M. I. Vázquez, Isobaric Vapor-Liquid Equilibria of Trichloroethylene with 1-butanol and 2-butanol at 20 and 100KPa, J. Chem. Eng. Data, v.41, 89-92,1996.

[10]   J. M. Mollerup and M. L. Michelsen, Calculation of Thermodynamic Equilibrium Properties, Fluid Phase Equilibria, 74, 1-15, 1992.

[11]   M. L. Michelsen and H. Kistenmacher, On Composition-Dependent Interaction Coefficients, Fluid Phase Equilibria, 58, 229-230, 1990.